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(19)

(54) PHOTOPOLYMERISABLE COMPOSITIONS

(71) We, UCB, of 4, Chaussée de Charleroi, Saint-Gilles-lez-Bruxelles, Belgium, A Body Corporate organised under the laws of Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new photopolymerisable compositions which are useful as varnishes and printing inks which can be cured by the action of ultra-violet rays, particularly as offset, letterpress, gravure, flexographic, copperplate printing and silk screen varnishes and printing inks.

One particularly advantageous application of the compositions of the present invention is in the field of inks which are polymerisable by ultra-violet rays and which hereinafter, for the sake of brevity, will be referred to as UV inks; these inks do not contain any solvents and dry and harden by the action of ultra-violet rays. In this particular case, very thin pigmented or coloured layers of these inks are applied to the paper and precisely because of the extreme thinness applied, allow sufficiently deep penetration of UV radiation to initiate photopolymerisation with a very high initiation speed.

Solventless inks are of interest in the fight against pollution. Conventional printing inks which dry by the application of heat contain, in fact, up to 45% of hydrocarbons, which are eliminated in ovens. The solvents are discharged to the atmosphere, together with the combustion gases. This pollution can be avoided by the expensive installation of catalytic or thermal post-combustion devices.

The use of UV inks reduces the encumbering of the workshop equipped with sheet-fed presses. Dried UV inks have better mechanical strength and chemical resistance together with a considerably increased drying speed, thus leading to a reduction of the time required before finishing, with a reduction of stocks of printed material in course of production and the elimination of the use of anti-set-off powders, which give rise to premature wear of certain parts of the press and entail difficulties in subsequent processing, for example during lamination.

The drying of inks, varnishes or lamination bonding products by ultra-violet irradiation is a known technique which has already been described in numerous patents. Nevertheless, the quality of the commercially available products has retarded their adoption by the graphic arts industry concerned with publication, production of packings, printing of textiles and decoration of various supports. In particular, some known UV inks have insufficient stability to storage or unacceptable drying, while others have good drying properties but, even more than those first mentioned, are characterised by severe difficulties in obtaining the water/ink balance in the offset process; these difficulties may even entail scumming or intensive tinting. Furthermore, reproducibility between various production batches must be considered inadequate because of the absence of definitions of physical and chemical characteristics (or control standards) which must be respected by the unsaturated prepolymers and the unsaturated oligomers or monomers forming part of the composition of these inks.

An improvement of binding power, resulting in better wetting of the pigments and good rheological behaviour and offset character, are obtained by incorporating fatty radicals.

Nevertheless, conventional technical methods of esterification or transesterification entail temperature and reaction time conditions under which the acrylic unsaturations must be protected by high contents of inhibitors, which are subsequently eliminated by laborious and expensive techniques.

The binders used in the present invention can be obtained under very mild conditions in the absence of solvents and high amounts of inhibitors and no longer require subsequent purification.

The compositions according to the present invention are perfectly suitable as offset, letterpress and flexographic inks and also as inks used for copperplate printing, gravure and silk screen printing, which are dried by UV radiation.

Thus, according to the present invention, there is provided a composition photopolymerisable by irradiation with ultra-violet light, which comprises:

1) a photopolymerisable binder, which is the reaction product of

(A) a di- and/or tri-isocyanate selected from (a) a di- or triisocyanate derived from a dimer or trimer obtained by dimerisation or trimerisation of a C_{18} unsaturated monobasic fatty acid, and (b) a urethane prepolymer having two or three free isocyanate groups, which is the reaction product of a di-isocyanate with a di- or triester of ricinoleic acid, and

(B) an acrylate containing at least two

$$CH_2=CH—COO—$$

radicals and at least one free hydroxyl group,

said photopolymerisable binder containing, on average, from 4 to 15

$$CH_2=CH—COO—$$

groups per molecule, and

2) at least one photoinitiator and/or photosensitiser.

In addition to the two essential ingredients of the photopolymerisable composition, the photopolymerisable binder and the photoinitiator or photosensitiser, said composition may also contain at least one inert polymer or plasticiser, copolymerisable monomer, oligomer or polymer, pigment or filler and at least one additive for ultra-violet varnishes and inks in amounts as specified hereinafter.

I. Photopolymerisable binder.

The photopolymerisable composition preferably contains 10 to 90% by weight of the photopolymerisable binder, which is the reaction product of compounds (A) and (B) defined above. In order to obtain UV inks having a high drying speed, this binder must contain, on average, from 4 to 15 and preferably from 4 to 9

$$CH_2=CH—COO—$$

groups per molecule.

Examples of the di- and triisocyanates (A) are in particular:

(a) the di- and/or triisocyanate derived from a dimer and/or trimer fatty acid obtained by controlled polymerisation of a C_{18} unsaturated monobasic fatty acid, for example the commercial product DDI 1410 sold by General Mills Chemicals Inc., which is the diisocyanate of a C_{36} dibasic acid obtained by controlled dimerisation of a C_{18} unsaturated monobasic fatty acid.

(b) the urethane prepolymers with two or three free isocyanate groups obtained by reacting a diisocyanate with a di- or triester of ricinoleic acid, such as castor oil (ricinoleic acid triglyceride), the diester of ricinoleic acid with ethylene glycol, etc. Products of this kind are marketed by the Baker Castor Oil Co. under the trade mark "Vorite". Thus "Vorite 63" used in the following Examples is a prepolymer obtained by reacting a mixture of castor oil and propylene glycol mono-ricinoleate with toluylene diisocyanate, the prepolymer obtained containing 14.4% NCO, a density at 25°C. of 1.113, a molecular weight of 288 and a Gardner coloration of 3.

The following are examples of acrylates (B) containing at least two

$$CH_2=CH—COO—$$

radicals and at least one free OH group:

(a') partial acrylic esters of aliphatic polyhydric alcohols containing at least three hydroxyl groups, such as pentaerythritol triacrylate as well as the partial acrylic esters of di- or tri-pentaerythritol. The product "Petia" sold by UCB and used in the following Examples is a mixture of 60—65% by weight pentaerythritol triacrylate and 35—40% by weight pentaerythritol tetraacrylate;

(b') partial acrylic esters of poly(oxyalkylene) derivatives of aliphatic polyhydric alcohols containing at least three hydroxyl groups, such as Pluracol SP 760 pentaacrylate used in the following Examples ("Pluracol SP 760" is the addition product of 12 moles ethylene oxide to 1 mole sorbitol having a molecular weight of about 760 and sold by Wyandotte Paint Products Co.);

(c') partial acrylic esters of polyesters containing at least three hydroxyl groups, such as the condensation product of 1 mole adipic acid with 2 moles trimethylolpropane and 3 moles acrylic acid; the condensation product of 1 mole maleic anhydride with 2 moles "Pluracol PeP 450" (addition product of 7 moles ethylene oxide to 1 mole pentaerythritol having a molecular weight of about 450) and 5 moles acrylic acid, etc.; ("Pluracol" is a Registered Trade Mark);

(d') the products of the reaction of polyepoxides with acrylic acid containing at least one free OH group, for example the reaction product of bisphenol A diglycidyl ether (marketed by the Dow Chemical Co. under the trade mark "D.E.R. 330" and by Shell under the trade mark "Epon" 827) with acrylic acid or the like.

The di- or tri-isocyanates (A) and the acrylates (B) are either known raw materials available commercially or can be prepared by known processes. With more particular regard to the acrylates (B), it is to be understood that the acrylic acid used in preparing the acrylates can be replaced by its functional derivatives, such as the acid halides (preferably chloride), the acid anhydride or its lower alkyl esters (in this latter case, transesterification is effected instead of esterification).

The binders constituted by the reaction product of the di- and tri-isocyanates (A) with the acrylates (B) can be prepared by an extremely simple process not requiring complicated equipment. It consists in heating the di- and/or triisocyanate (A) and the acrylate (B) at a temperature of 20 to 100°C., preferably of 60 to 70°C., in the presence of a catalyst, such as dibutyl tin dilaurate, triethylene diamine or the like, in such a manner that for one NCO group equivalent there is at least one hydroxyl group equivalent. If the process is carried out below the preferred temperature range, the reaction time is longer, whereas if the process is carried out above this range, the danger of premature polymerisation of the unsaturated acrylic groups increases as a function of the temperature. Since the reaction is exothermal, provision should be made to keep the temperature of the reaction medium within the preferred range of 60—70°C. by appropriate cooling. The end of the reaction is indicated by the disappearance of the NCO groups, which can be verified either by the di-*n*-butylamine titration method (P. Wright, Solid Polyurethane Elastomers, pub. McLaren & Sons, London, 1969, page 84) or by infra-red spectrophotometry (disappearance of the characteristic band of the NCO group at 2260 cm^{-1}). At the end of the reaction, a small amount of a lower alcohol, such as *n*-propanol, may be added, if desired, in order to effect the complete disappearance of the free NCO groups. The reaction generally takes from 30 minutes to 8 hours and, on average, about 2 hours.

The following are examples of the photopolymerisable binder (I):

1) the product of the reaction of DDI 1410 (described above) with Petia (described above), in the proportion of 1 NCO equivalent of DDI to from 1.2 to 1.8 OH equivalents of Petia;
2) the product of the reaction of Vorite (described above) with the above-mentioned Petia in the proportion of 1 NCO equivalent of the former to 1.8 OH equivalent of the latter;
3) the product of the reaction of the above-mentioned DDI 1410 and Pluracol SP 760 pentaacrylate (described above) (the latter containing 0.91 milliequivalent of OR/g.) in the proportion of 1 NCO equivalent of the former to 1.1 OH equivalent of the latter;
4) the product of the reaction of the above-mentioned DDI 1410 with a hydroxylated acrylic polyester, in the proportion of 1 NCO equivalent of the former to 1.5 OH equivalent of the latter (the hydroxylated acrylic polyester used above is obtained by reacting 1 mole of adipic acid with 2 moles of trimethylolpropane and 3 moles of acrylic acid; it contains 5.5 milliequivalents of acrylic unsaturation/g. and 1.9 milliequivalents of OH/g.);
5) the product of the reaction of the mentioned DDI 1410 with "Derakane", in the proportion of 1 NCO equivalent of the former to 1.4 OH equivalent of the latter ("Derakane" is the product of the reaction of 2 moles of acrylic acid with bisphenol A diglycidyl ether; its molesule weight is about 485 and it contains 4 milliequivalents of OH/g. and 4 milliequivalents of acrylic unsaturation/g.; it is sold by the Dow Chemical Co.). ("Derakane" is a Registered Trade Mark.)

The binders constituted by the reaction products of the di- and tri-isocyanates (A) with the acrylates (B) are waxy to liquid substances, the viscosity of which, at ambient temperature, is between a few poises and a few thousand poises. They are colourless to dark brown, depending upon the quality of the raw materials and the operating conditions used for the synthesis thereof. They have a good solubility in aromatic solvents, ketones, esters and the like and also in mono- and polyfunctional acrylic and vinyl monomers. Their vapour pressure at ambient temperature is practically negligible.

The advantage of the binders constituted by the reaction products of the di- and triisocyanates (A) with the acrylates (B) is that the equilibrium between the lipophilic part and the hydrophilic part of the molecule can be varied at will (see Example 1), which is particularly important in the formulation of UV offset inks. Unlike the binding agents at present used in UV offset inks, the equilibrium between the ink and the fountain solution when using the binders which are the reaction products of (A) and (B) can easily be achieved and maintained in the press, even after a stop in the printing. Isopropanol

contents of the order of from 10 to 25% by weight may be used without disadvantage in the fountain solutions. Among the binders which are the reaction products of (A) and (B), the best offset behaviour is obtained with those with a hydroxyl index between 20 and 50. These binders have the particular advantage of being completely inert to most of the ink distribution rollers and to most of the blankets which transfer the ink from the plate cylinders to the printing support.

II. Inert polymers and plasticisers.

In addition to the above-described photopolymerisable binder, the photopolymerisable compositions of the present invention may contain from 0 to 40% by weight of inert polymers and plasticisers. The following are mentioned as particular examples of inert polymers: polyolefins, polystyrene, polyalkyl acrylates, polyvinyl chloride, polyvinyl acetate, polyethers, polyamides, saturated polyesters, alkyd resins, epoxy resins, urea-formaldehyde resins, aryl sulphonamide-formaldehyde resins, terpene - phenol resins, polyvinyl alkyl ethers, chlorinated rubber, cellulose esters (acetopropionate, acetobutyrate and the like), copolymers of vinyl chloride with vinyl acetate, maleic esters, vinylidene chloride, vinyl esters and the like.

The inert plasticisers which can be added to the photopolymerisable compositions of the present invention are esters of organic or mineral acids, such as *o*-, iso- or terephthalic acid, adipic acid or the like, with mono- or polyhydric aliphatic or aromatic hydroxylated compounds, such as butanol, 2-ethylhexanol, triethylene glycol or the like. Epoxidised oils, chlorinated hydrocarbons, chlorinated naphthalenes or the like, may similarly be used as plasticisers.

The inert plasticisers and polymers are added in order to adapt or modify printability characteristics, final appearance (gloss) and the properties of the ink films obtained.

III. Copolymerisable monomers, oligomers and polymers.

These represent from 0 to 40% by weight of the photopolymerisable compositions of the present invention.

The copolymerisable monomers and alogimers which can be added to the compositions of the present invention are used when it is required to modify the viscosity, flow limit or tack character, with a view to adapting the resulting product to various applications and/or technical uses. They are, in particular, used to lower the viscosity of the product obtained. At the moment of polymerisation, these oligomers copolymerise with the binders above-described and, therefore, form a permanent part of the compositions obtained in this manner. In order to avoid a reduction of the speed of drying under ultra-violet radiation, monomers or aligomers carrying acrylic unsaturations are used. The monomers can be acrylates and polyacrylates of polyols, such as trimethylolpropane triacrylate.

For offset inks, monomers are selected from products with a boiling point higher than 230°C. at atmospheric pressure. Examples of copolymerisable oligomers include the di-, tri- and polyacrylates of hydroxylated products which have been obtained by condensing ethylene or propylene oxide or ε-caprolactone on to glycerol, trimethylolpropane, pentaerythritol, sorbitol or the like, such as the "Tercarol G 310" triacrylate used in the following Examples.

As an example of copolymerisable polymers, mention is made of the polymers with a molecular weight lower than 5000 and which carry acrylic groups at the ends of the chains or at a lateral position along the chain. Polymers of this kind are well known and have been described with a wide variety of structures, such as polyesters, acrylics, polyepoxides, polyurethanes and the like.

IV. Pigments and fillers.

The pigments and fillers for the UV inks of the present invention are added in order to impart colorimetric properties. An ink may contain, for example:

from 0 to 30% by weight of organic pigments,
from 0 to 25% by weight of carbon black,
from 0 to 60% by weight of inorganic pigments,
from 0 to 50% of fillers,

the total amount of pigment and fillers being between 10 and 60% by weight, in the case of UV inks; it is, however, 0% by weight in the case of an overprint varnish. These pigments and fillers must neither retard nor inhibit the photopolymerisation of the photopolymerisable binder. They must neither react chemically with the photoinitiator or initiators and/or photosensitiser or photosensitisers nor adsorb them physically.

The organic pigments can be selected from the products set out in the Colour Index, the absorption of which, in the wavelengths between 200 and 500 nanometers, is as low as possible.

The utilisation of masking mineral pigments may be necessary for the production of certain inks, for example in the case of offset inks intended for tinplate printing. Titanium oxides, lead and zinc chromates and molybdates and bronze and aluminium powders may be mentioned as examples of masking pigments. It is obvious that UV absorption by these opacifying pigments is higher than with organic pigments which

are transparent to UV and that inks formulated on the basis of these opacifying pigments require higher irradiation energy (expressed in watts per cm² of printed surface). In other words, in order to obtain the same drying rate, it is necessary to increase the number of UV radiators.

The fillers are selected so as to have a minimum absorption in the range from 200 to 500 nanometers. These include precipitated, or micronised magnesium or calcium carbonate (calcite, aragonite or the like), barium sulphate or calcium sulphate (baryta, blanc fixe (barium sulphate) or the like), micronised hydrated magnesium or potassium silicoaluminate, micronised magnesium silicate, precipitated alumina hydrate, asbestine, micronised or non-micronised talc or the like.

V. Photoinitiators and photosensitisers.

These are preferably used in amounts of from 1 to 15% by weight in the photopolymerisable compositions of the present invention. They make it possible to polymerise these compositions under the influence of radiation, the wavelengths of which are between 200 nm and 500 nm. The photosensitisers supply to all the molecules containing 1 or more unsaturations, or to the initiator, a part of the energy transmitted by light. By means of the unsaturated system or systems or of a photoinitiator, the photosensitisers produce free radicals or ions which initiate the polymerisation or the cross-linking of the composition.

The photoinitiators are essentially chemical substances belonging to the following groups:

compounds containing carbonyl groups, such as pentanedione, benzil, piperonal, benzoin, and its halogenated derivatives, benzoin ethers, anthraquinone and its derivatives, *p,p'* - bis - (dimethylamino) - benzophenone, benzophenone, dibenzosuberone, camphoquinone and the like;

compounds containing sulphur or selenium, such as the di- and polysulphides, xanthogenates, mercaptans, dithiocarbamates, thioketones, β - naphthoselenazolines and the like;

organic peroxides, such as benzoyl peroxides, *t*-butyl peroxide and the like;

compounds containing nitrogen, such as the azonitriles (for example azo - bis - isobutyronitrile), diazo compounds, diazides, derivatives of acridine, phenazine, quinoxaline, quinazoline, and oxime esters, for example 1 - phenyl - 1,2 - propanedione 2 - [O - (benzoyl)oxime] or the like;

halogenated compounds, such as halogenated aldehydes and ketones, methylaryl halides, sulphonyl halides and dihalides and the like;

photoinitiator dyestuffs, such as diazonium salts, azoxy - benzenes and derivatives, rhodamines, eosines, fluorescein, acriflavine and the like.

The photosensitisers belong to the following groups: ketones and their derivatives, carbocyanines and methines, polycyclic aromatic hydrocarbons, such as anthracene, and dyestuffs, such as xanthenes, safranines and acridines.

For further information regarding the photosensitizers and photoinitiators which can be used in the present invention, reference is made to the following: G. Delzenne, Ind. chim. Belge, *24*, (1959) 739—64; J. Kosar, Light Sensitive Systems, New York, Wiley, 1965; N. J. Turro, Molecular Photochemistry, New York, Benjamin Inc., 1967; and H. G. Heine, H. J. Rosenkranz, H. Rudolph, Angew. Chem. *84*, 1032/1972.

VI. Conventional or special additives for ultra-violet varnishes and inks.

When present, these are used in amounts of from 1 to 20% by weight. the following are examples of these additives:

known stabilisers, antioxidants, viscosity modifying agents and flowing agents;

chain-transfer agents serving to accelerate radical polymerisation once it has been initiated; examples of these agents include the di- and triamines, alkanolamines. monoalkyldialkanolamines and dialkylmonoalkanolamines, morpholine and its derivatives, the polyamines, N-phenyl-glycine and its derivatives, N,N' - dimethylaminoethanolamine monoacrylate, N - methyldiethanolamine diacrylate, triethanolamine triacrylate and the like;

polymerisation inhibitors intended to provide storage stability, for example quinones, hydroquinones, substituted phenol derivatives, primary aromatic amines, copper compounds and the like;

waxes, the purpose of which is to assist the obtaining of scratch-proof hardened films; these waxes may be natural, such as candelilla wax or Carnauba wax, or synthetic such as polyethylene wax, polypropylene wax, paraffin wax, chlorinated paraffin waxes, chlorinated naphthalenes and the fluorinated waxes.

The following Examples, in which the parts are parts by weight unless otherwise stated, are given for the purpose of illustrating the present invention, Examples 1 to 4 illustrating the preparation of binders used in the present invention:—

Example 1

The proportions by weight, indicated in the Table below, of the lipophilic DDI 1410 (described above) and hydrophilic Petia (described above) are introduced into a double-walled 1-litre glass reactor equipped

with a thermometer and an anchor type agitator.

0.25 part of dibutyl tin dilaurate is added per 100 parts of the mixture. The mixture is agitated in the open and at atmospheric pressure and brought to 65°C. until the isocyanate groups have disappeared, which takes about 2 hours.

The viscosity in poises at 25°C. and the hydroxyl index of the different binders obtained are then measured.

TABLE

Petia	DDI 1410	Viscosity	Hydroxyl index
74	26	65	48
72	28	92	40
70	30	122	36
68	32	190	28
66	34	225	22

When the logarithm of the viscosity and the OH index of the above binders are plotted against the Petia content, straight lines are obtained (see the Figure of the accompanying drawing). By means of these lines, it is possible to determine the composition of a binder, the viscosity of which is most suitable for use as UV ink or varnish on a given printing machine.

Example 2

This Example illustrates the choice of a binder (amongst those of the preceding Example) as a function of the required viscosity for use on an industrial scale. In A) below, the binder was chosen which would have a viscosity of about 200 poises, which is suitable for offset inks for sheet-fed machines, whereas in B) below, the binder was chosen which would have a viscosity of about 80 poises, which is suitable for offset inks for web presses.

A) 68 kg. of the above-mentioned Petia, containing 2.2 milliequivalents of OH/g., and 32 kg. of the above-mentioned DDI 1410 are introduced into a double-walled stainless steel reactor with a capacity of 150 litres equipped with an anchor type agitator and an automated heated control system. The Petia is stabilised with 1500 ppm of hydroquinone monomethyl ether.

The mixture is brought to 65°C., while agitating, and 5 portions, each of 0.05 part, of dibutyl tin dilaurate are then introduced every 20 minutes.

The reaction is allowed to proceed at this temperature until the disappearance of the isocyanate groups, i.e. about 1 hour. A sample of this binder gives the following values:

Viscosity at 25°C. =200 poises
OH index = 25.

B) Exactly the same method of operation is adopted as in A), but using 72 kg. of Petia and 28 kg. of DDI 1410. A binder is obtained which has the following characteristics:

Viscosity at 25°C. =80 poises
OH index =41

Example 3

The following are introduced into the same reactor as was used in Example 1:

31 parts by weight of Vorite 63 (see above)
69 parts by weight of the aforesaid Petia
0.25 parts of triethylene diamine.

The binder has the following characteristics:

Viscosity at 25°C. =2000 poises
OH index = 24

Example 4

The following products are reacted at 70°C. for 2 hours in the same reactor as in Example 1:

1000 g. of "Pluracol" SP 760 (described above) pentaacrylate containing 0.91 milliequivalent of OH/g.
240 g. of the aforesaid DDI 1410
2.5 g. of dibutyl tin dilaurate.

The binder thus obtained has the following characteristics:

Viscosity at 25°C. =156 poises
OH index = 6

Example 5

Offset ink for web press

An offset ink is prepared from the following constituents:

15 parts of phthalocyanine blue (Colour Index Pigment Blue 15)
68 parts of the binder of Example 2B
6 parts of trimethylolpropane triacrylate
5 parts of dioctyl phthalate
5 parts of benzoin isobutyl ether
1 part of polyethylene wax, product PA-520 of Farbwerke Hoechst).

The ink is applied in a thickness of about 1 micron to a strip of paper. The speed is determined at which set-off occurs when the strip of paper is passed at various speeds, at a distance of 7.5 cm., under a UV lamp of "Hanovia" type No. 6525 A 431 with an arc length of 62.5 cm. and a power of 5 kW (medium pressure mercury lamp).

("Hanovia" is a Registered Trade Mark.)

Set-off occurs at 3.0 metres per second

and the hardened ink becomes scratch-proof 2 hours after irradiation.

In four-colour printing on a rotary press equipped with 3 UV lamps of the type described, the ink dries at a speed of 300 metres per minute.

Example 6

Offset ink for sheet-fed machines

This is prepared from the following constituents:

16 parts of benzidene yellow AAMX (Colour Index Pigment Yellow 17)
70 parts of the binder of Example 2A
3 parts of trimethylolpropane triacrylate
5 parts of dioctyl phthalate
5 parts of a mixture of benzophenone and Michler's ketone (ratio 6:1 by weight)
1 part of polyethylene wax (PA-520 of Farbwerke Hoechst).

When the ink is tested as in Example 5, set-off occurs at 3.5 metres per second.

In four-colour printing on a sheet-fed press provided with three UV lamps of 80 W/cm, it was possible to work at a rate of 8000 sheets per hour.

Example 7

UV varnish

This was prepared from the following constituents:

54 parts of the binder of Example 4
15 parts of N - methyl - diethanolamine diacrylate
20 parts of Tercarol G 310 triacrylate
10 parts of benzophenone
1 part of polyethylene wax (product PA-520 of Farbwerke Hoechst).

(Tercarol G 310 is a condensation product of 3 moles of propylene oxide on 1 mole of glycerol, which has a molecular weight of about 310.)

When the varnish is applied in a layer of from 0.5 to 1 micron on a strip of paper printed as in Example 5, it hardens at a speed of 2.5 metres per second when passed under an 80 W/cm lamp.

The hardened varnish is colourless, adheres well to the ink and it has a good gloss.

WHAT WE CLAIM IS:—

1. A composition photopolymerisable by irradiation with ultra-violet light, which comprises:

1) a photopolymerisable binder, which is the reaction product of

(A) a di- and/or tri-isocyanate selected from (a) a di- or triisocyanate derived from a dimer or trimer obtained by dimerisation or trimerisation of a C_{18} unsaturated monobasic fatty acid, and (b) a urethane prepolymer having two or three free isocyanate groups, which is the reaction product of a diisocyanate with a di- or triester of ricinoleic acid, and

(B) an acrylate containing at least two

$$CH_2=CH—COO—$$

radicals and at least one free hydroxyl group,

said photopolymerisable binder containing, on average, from 4 to 15

$$CH_2=CH—COO—$$

groups per molecule, and

2) at least one photoinitiator and/or photosensitiser.

2. A composition according to claim 1, wherein the photopolymerisable binder contains, on average, from 4 to 9

$$CH_2=CH—COO—$$

groups per molecule.

3. A composition according to claim 1 or 2, wherein the acrylate (B) is a partial acrylic ester of a compound selected from aliphatic polyhydric alcohols containing at least three hydroxyl groups, poly(oxyalkylene) derivatives of aliphatic polyhydric alcohols containing at least three hydroxyl groups and polyesters containing at least three hydroxyl groups.

4. A composition according to claim 1 or 2, wherein the acrylate (B) is a reaction product of a polyepoxide with acrylic acid containing at least one free hydroxyl group.

5. A composition according to any of the preceding claims, which comprises 10 to 90% by weight of the photopolymerisable binder (1) and 1 to 15% by weight of the photoinitiator or photosensitiser (2).

6. A composition according to any of the preceding claims, which also contains up to 40% by weight of at least one inert polymer and/or plasticiser.

7. A composition according to any of the preceding claims, which also contains up to 40% by weight of at least one copolymerisable polymer, oligomer and/or monomer.

8. A composition according to any of the preceding claims, which also contains 1 to 20% by weight of at least one additive for ultra-violet varnishes and inks.

9. A composition according to any of the preceding claims, which also contains up to 60% by weight of at least one pigment and/or filler.

10. A composition according to any of the preceding claims, substantially as hereinbefore described and exemplified.

11. A varnish curable by irradiation with ultra-violet light, the formulation of which comprises a composition according to any of claims 1 to 8.

12. An offset printing ink curable by irradiation with ultra-violet light, the formulation of which comprises a composition according to claim 9 or 10.

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1493134 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*